P145

Elastic and piezoelectric properties of diphenylalanine microtubes with different filling of nanochannels

V. Yuzhakov[1], A. Nuraeva[1], P. Zelenovskiy[1,2], D. Chezganov[1], A. Kholkin[1,2], V. Shur[1]

[1]*School of Natural Sciences and Mathematics, Ural Federal University, 620000, Ekaterinburg, Russia*
vladimir.yuzhakoff@mail.ru

[2]*Department of Physics & CICECO − Aveiro Institute of Materials, University of Aveiro, 3810-193, Aveiro, Portugal*

Self-assembled micro- and nanotubes of diphenylalanine ($C_{18}H_{20}N_2O_3$, FF) represent advanced functional biomaterial for developing new medical equipment [1], such as laboratory-on-chip, due to its outstanding piezoelectric [2] and mechanical [3] properties. After the self-assembly in aqueous solution water molecules remain inside the nanochannels and stabilize its structure [4]. However, the possibility of water substitution in nanochannels by other molecules and its effect on physical properties of FF microtubes still was not studied.

In this work we investigated the effect of nanochannels filling on piezoelectric and elastic properties of FF microtubes. The studied microtubes were grown from a solution of FF-monomer (Bachem AG, Switzerland) in mixture of 1,1,1,3,3,3-hexafluoro-2-propanol with water and then were dried at 80 °C for different times in a muffle furnace to empty the nanochannels. The consequent filling of nanochannels by water or ethanol molecules was carried out by keeping the empty microtubes in water or ethanol vapor for two weeks. Average concentration of water molecules in the microtubes was detected by confocal Raman microscope Alpha 300AR (WITEC GmbH, Germany) according to the earlier described procedure [5]. Young's modulus and micro-hardness were measured locally using NanoScan-4D scanning nano-hardness tester (FSBI TISNCM, Russia). The piezoelectric coefficient was measured using a scanning probe microscope MFP-3D (Asylum, USA).

As-grown FF microtubes demonstrate a bimodal distribution of the Young modulus values with characteristic values of 10 and 25 GPa and piezoelectric response of about 35 pm/V. Analysis of Raman spectra showed that the Young's modulus of 10 GPa corresponds to microtubes with 12 water molecules in the structural unit. Drying of microtubes leads to decrease of Young's modulus and piezoelectric response. Restoring the microtubes in water or ethanol vapor leads to increasing of Young's modulus values back to bimodal distribution with characteristic values that are close to values of initial (as-grown) tubes. Thus, water or ethanol molecules can enter the nanochannels in FF microtubes and allow recovering their elastic properties. However piezoelectric coefficient d_{15} of the refilled microtubes does not restored. The origin of this contradiction is not clear yet.

The research was carried out using the equipment of Ural Center for Shared Use "Modern Nanotechnologies", Ural Federal University, under financial support by Russian Science Foundation (grant № 18-72-00052).

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